OVERALL REACTION RATE AND STOICHIOMETRY FOR
THERMAL DECOMPOSITION OF HYDRAZINE

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ABSTRACT

An asymptotic analysis of the Eberstein-Glassman kinetic mechanism for the thermal decomposition of hydrazine is carried out. It is shown that at temperatures near 800°K and near 1000°K, and for hydrazine molar fractions of the order of unity, 10^{-1} and 10^{-2} , the entire kinetics reduces to a single, overall reaction.

Characteristic times for the chemical relaxation of all active, intermediate species produced in the decomposition, and for the overall reaction, are obtained. Explicit expressions for the overall reaction rate and stoichiometry are given as func tions of temperature, total molar concentration (or pressure) and hydrazine molar fraction. Approximate, patched expressions can then be obtained for values of temperature and hydrazine molar fraction between 750 and 1000°K, and 1 and 10^{-3} respectively.

RESUME

On a développé un étude asymptotique du mecanisme cinéti-que de Eberstein-Glassman pour la décomposition thermique de l'hydrazine. On montre que ce mecanisme peut se reduire à une reaction globale si la temperature est près de 800°K ou de 1000°K, et la fraction molaire de l'hydrazine est de l'ordre de l'unité, 10^{-1} ou 10^{-2}.

Les temps caracteristiques correspondents a la relâchement chimique pour toutes les espèces intermediares et pour la réac-tion globale ont été determinées. On a calculé aussi des expres-sions pour la vitesse de réaction globale ainsi que la stoechio-métrie, en function de la température, concentration molaire total (ou pression) et fraction molaire de l'hydrazine. Des ex-pressions valables pour les valeurs des températures compris parmis 750° et 1000°K et fractions molaires parmis 1 et 10^{-3} peuvent être obtenues.

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1. INTRODUCTION

Low thrust, monopropellant engines based on the catalytic decomposition of hydrazine have been operational, for some time, on board spacecrafts. However, for thrusts below 0.1 lbf say,it is difficult to achieve reliable catalytic engines. For that thrust range, propulsion systems based on hydrazine thermal decomposition have been lately proposed[1-3]. A basic aspect of such systems is a homogenous, gas phase, complex kinetics.

In an engine this chemical kinetics is coupled to gas dynamic processes, and as consequence basic analyses of thruster performance become difficult. Fortunately, a single, overall reaction (stoichiometry and reaction rate) can substitute for the entire kinetic mechanism, under some conditions: If all intermediate radicals produced in the decomposition reach equilibrium with hydrazine in a time much shorter than the overall chemical time for transformation of hydrazine into products, radical concentrations become fixed functions of hydrazine concentration - and of temperature and pressure -, in the slower evolution of these variables. If then the characteristic residence or mechanical time for the engine is large compared with the radicals relaxation time, in particular if mechanical and overall chemical times are comparable, an overall kinetics may be used in the gas dynamics equations for the engine.

The purpose of this paper is threefold. Firstly to find out whether indeed an overall kinetics may exist, that is, to compare overall chemical and radicals relaxation times. Secondly to provide values for these times (in order to allow later comparison with mechanical times in engines) and to obtain analytical expressions for overall reaction rate and stoichiometry. Finally, to test the validity of some of the kinetics proposed for the thermal decomposition of hydrazine;[4-11] we shall consider here the detailed kinetic mechanism set forth by Eberstein and Glassman[11] for the temperature interval between 750 and 1000°K which appears to be of main importance for engine analysis.

In a recent paper Urrutia[12] used that mechanism to obtain overall results for the decomposition of highly diluted hydrazine at temperatures near 1000°K. In the present work we consider temperatures near both 800°K and 1000°K, with initial hydrazine molar fractions of order of unity, as would be the case in a real engine. In the next section, we discuss the formulation of the problem. In Secs. 3 and 4 we present the results for 1000°K and 800°K respectively. A discussion of these results is given in Sec.5.
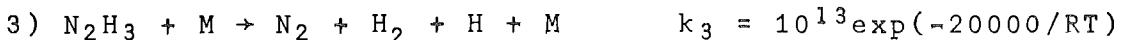
2. FORMULATION OF THE PROBLEM

The kinetic mechanism proposed by Eberstein and Glassman for hydrazine decomposition involves species N_2H_4 , NH_2 , NH , N_2H_3 , H , NH_3 , N_2 , H_2 , (numbered 1 to 8) and ten elementary reactions:
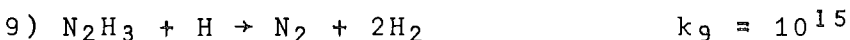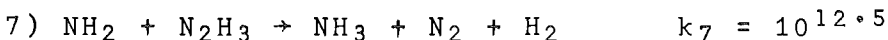
Initiation

1) $N_2H_4 + M \rightarrow 2NH_2 + M$ $\qquad$ $k_1 = 10^{19}\exp(-60000/RT)$

Propagation

2) $N_2H_4 + NH_2 \rightarrow N_2H_3 + NH_3$ $\qquad$ $k_2 = 10^{12}\exp(-7000/RT)$

3) $N_2H_3 + M \rightarrow N_2 + H_2 + H + M$ $\qquad$ $k_3 = 10^{13}\exp(-20000/RT)$

4) $N_2H_4 + H \rightarrow NH_2 + NH_3$ $\qquad$ $k_4 = 10^{13}\exp(-7000/RT)$

$\hfill (1)$

Chain branching

5) $N_2H_3 + M \rightarrow NH + NH_2 + M$ $\qquad$ $k_5 = 10^{12.9}\exp(-18000/RT)$

6) $N_2H_4 + NH \rightarrow NH_2 + N_2H_3$ $\qquad$ $k_6 = 10^{14}\exp(-10000/RT)$

Termination

7) $NH_2 + N_2H_3 \rightarrow NH_3 + N_2 + H_2$ $\qquad$ $k_7 = 10^{12.5}$

8) $2N_2H_3 \rightarrow 2NH_3 + N_2$ $\qquad$ $k_8 = 10^{12}$

9) $N_2H_3 + H \rightarrow N_2 + 2H_2$ $\qquad$ $k_9 = 10^{15}$

10) $2NH_2 \rightarrow N_2H_4$ $\qquad$ $k_{10} = 10^{12.5}$


where all k's are measured in cc/mole-sec.

If $w_{i\alpha}$ is the rate of production (moles per unit time and unit volume) of the ith species due to the αth reaction, which fol lows from the above mechanism, the continuity equation for the ith species in a general situation reads

$$\frac{DY_i}{Dt} + \frac{1}{\rho}(\nabla \cdot \rho Y_i \overline{v}_{di}) = \frac{M_i}{\rho} \sum_\alpha w_{i\alpha} \qquad (2)$$

where Y_i, $\overline{v}_{di}$ and M_i are the ith mass fraction, diffusion velocity and molar mass respectively. The left-hand side of Eq.(2) is of the order of Y_{ic}/t_m, Y_{ic} being a characteristic value for Y_i and t_m a characteristic mechanical or residence time. The right-hand side contains negative terms arising from the consumption of the ith species in reactions where it enters as a reactant; such terms are of the order of Y_i^n/t_{ci} (n=1 or 2) where t_{ci} is a chemical time which depends on the concentrations of other species. The right side contains also positive terms due to the reactions where the ith species enters as a product; they are of the order of $1/t'_{ci}$ where t'_{ci} is another chemical time. For a very active species t_{ci} is so small that the species is consumed as soon as it is produced - so to speak -, that is,

$$\sum_\alpha w_{i\alpha} \simeq 0 , \qquad (3)$$

Y_i being very small. Equations (3) then provide expressions for Y_i , for all active species, as functions of reactants and main products. This eliminates the active species of the main evolution of the reaction and leads to simplified kinetics. In the present problem we expect species 2 to 5 to be very active in the above sense, so that an overall reaction would result;

$$N_2H_4 \rightarrow \alpha NH_3 + \beta N_2 + \gamma H_2 \ , \tag{4}$$

$$\alpha = 2(1-\beta) \quad , \quad \gamma = 3\beta - 1.$$
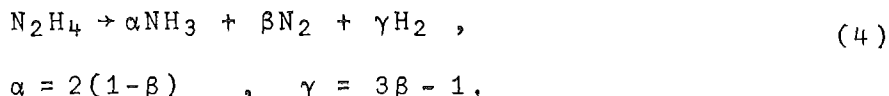
To find out whether radicals NH_2 , NH , N_2H_3 and H are indeed very active, and to determine the values of the various chemical times, of β (and thus of the heat of reaction), and of the overall reaction rate, it is then simplest to consider a constant volume and temperature, spatially uniform, hydrazine decomposition process. Equations (2) then become

$$\frac{dc_i}{dt} = \sum_\alpha w_{i\alpha} \tag{5}$$

where $c_i = \rho Y_i/M_i$ is the ith molar concentration. Especifically we have

$$\frac{dc_1}{dt} = -k_1 c c_1 - k_2 c_1 c_2 - k_4 c_1 c_5 - k_6 c_1 c_3 + k_{10} c_2^2$$

$$\frac{dc_2}{dt} = 2k_1 c c_1 - k_2 c_1 c_2 + k_4 c_1 c_5 + k_5 c c_4 + k_6 c_1 c_3$$
$$- k_7 c_2 c_4 - 2k_{10} c_2^2$$

$$\frac{dc_3}{dt} = k_5 c c_4 - k_6 c_1 c_3$$

$$\frac{dc_4}{dt} = k_2 c_1 c_2 - k_3 c c_4 - k_5 c c_4 + k_6 c_1 c_3 - k_7 c_2 c_4$$
$$- 2k_8 c_4^2 - k_9 c_4 c_5 \tag{5'}$$

$$\frac{dc_5}{dt} = k_3 c c_4 - k_4 c_1 c_5 - k_9 c_4 c_5$$

$$\frac{dc_6}{dt} = k_2 c_1 c_2 + k_4 c_1 c_5 + k_7 c_2 c_4 + 2k_8 c_4^2$$

$$\frac{dc_7}{dt} = k_3 c c_4 + k_7 c_2 c_4 + k_8 c_4^2 + k_9 c_4 c_5$$

$$\frac{dc_8}{dt} = k_3 c c_4 + k_7 c_2 c_4 + 2k_9 c_4 c_5.$$

Equations (5') are to be solved under initial conditions

$$c_1(t=0) = c_1\% = 0(1)$$
$$c_i(t=0) = 0 \quad , \quad i \neq 1 . \tag{6}$$

It may be now noticed that, due to the fact that NH_3 , N_2 and H_2 enter only as products in the Eberstein-Glassman mechanism, the first five equations in (5') are decoupled from the last three. A further essential simplification arises from the differences, of several orders of magnitude, existing between many rate constants. This allows the use of a (singular) perturbation method, essentially a multiple time-scale analysis, by making Eqs (5') nondimensional and ordering the terms in their right-hand sides in powers of a small number ε , equal to 10^{-2} say. The five ordinary differential equations for c_1 , c_2 ... c_5 may then be solved asymptotically by letting ε formally go to zero (although at the end of the analysis it must be set equal to 10^{-2}) and retaining dominant terms only.

However, since the rate constants appear multiplying some species concentrations, and these may change substantially as time evolves, it is clear that the relative importance of each term in those equations, changes with time. Thus there will exist several successive stages, different (hopefully few) terms being dominant at each stage. One then proceeds integrating in time the first five Eqs (5'), starting from conditions (6), and at each new stage the results from the previous stage allow to determine the new dominant terms. It should be noticed that the rate constants of some elementary reactions increase steeply from 750°K to 1000°K and therefore the selection of dominant terms, and thus the number and character of the time stages, will be clearly dependent on temperature.

In the next two sections we give the results of such an asymptotic analysis for temperatures around 1000°K and 800°K. Specifically, we give the characteristic (chemical) times and behaviour of the different stages found, and explicit formulae for β and dc_1/dt as functions of c_1 , T and P (pressure).

3. TEMPERATURE NEAR 1000°K

For $T \simeq 1000°K$ and $c_1\% = 0(1)$ five stages are found in the decomposition. The first four stages correspond to chemical relaxation of species NH_2 , NH , N_2H_3 and H . Transformation of hydrazine into NH_3 , N_2 and H_2 takes place in a fifth, much slower stage. Thus, at $T = 1000°K$, the Eberstein-Glassman mechanism leads to the existence of an overall kinetics.

There is first a stage with a characteristic time of the order of $(10^{-7}/P)$ sec - where P is measured in atmospheres -, in which NH relaxes to equilibrium through reactions 5 and 6, reaching a quasi-steady state. Next, there occurs relaxation of H through reactions 3 and 4, in a time of the order of $(10^{-6}/P)$sec. Then, in a time of the order of $(10^{-5}/P)$ sec, NH_2 relaxes through reactions 1 and 2. Finally, for times of the order of $(10^{-4}/P)$sec, N_2H_3 comes to equilibrium in reactions 2, 3, 5, 6, 8 and 9; simultaneously, reaction 4 becomes negligible and reactions 5 and 6

come into play in the quasi-steady state of NH_2.

Hydrazine decomposes in a much larger time, of the order of $(10^{-1}/P)$ sec, through reactions 1, 2 and 6; we thus have

$$\frac{dc_1}{dt} = w_1 \simeq - k_1 cc_1 - k_2 c_1 c_2 - k_6 c_1 c_3 \tag{7}$$

At this stage, from the preceding results, we also have

$$0 \simeq w_2 \simeq 2k_1 cc_1 - k_2 c_1 c_2 + k_5 cc_4 + k_6 c_1 c_3$$

$$0 \simeq w_3 \simeq k_5 cc_4 - k_6 c_1 c_3$$

$$0 \simeq w_4 \simeq k_2 c_1 c_2 - k_3 cc_4 - k_5 cc_4 + k_6 c_1 c_3 - 2k_8 c_4^2 - k_9 c_4 c_5 \tag{8}$$

$$0 \simeq w_5 \simeq k_3 cc_4 - k_9 c_4 c_5.$$

Using (8) in (7) we then find an explicit expression for the overall rate of decomposition of hydrazine, $\overline{w}_1$, as function of c_1, T and c, or alternatively c_1, T and P $(c = P/RT)$,

$$\frac{dc_1}{dt} \simeq \overline{w}_1 = - 3k_1 cc_1 \left[1 + \frac{1 + (1+2\phi)^{1/2}}{(1 - k_3/k_5)\phi} \right]$$

$$= -3 \frac{k_5}{k_8} (k_5-k_3) c^2 \frac{1}{2} \left[1 + (1+2\phi)^{1/2} + (1-k_3/k_5)\phi \right] \tag{9}$$

$$\simeq - 10^{14} \exp\left(- \frac{36000}{RT}\right) c^2 \frac{1}{2} \left[(1 + 2\phi)^{1/2} + 0.54\phi \right]$$

where

$$\phi = \frac{2k_1 k_8}{(k_5-k_3)^2} \frac{c_1}{c} \simeq 1.1 \times 10^6 \exp\left(- \frac{24000}{RT}\right) \frac{c_1}{c} . \tag{10}$$

We also find

$$\frac{c_2}{c} = 0(10^{-4}) , \quad \frac{c_3}{c} = 0(10^{-6}) , \quad \frac{c_4}{c} = 0(10^{-3}) , \quad \frac{c_5}{c} = 0(10^{-6}) . \tag{11}$$

In an engine we would then use $\overline{w}_1$ in

$$\frac{DY_1}{Dt} + \frac{1}{\rho} \nabla\cdot(\rho Y_1 \vec{v}_{d1}) = \frac{M_1}{\rho} \overline{w}_1 .$$

According to (4) the overall rates of production of NH_3, N_2 and H_2 would be

$$\overline{w}_6 \simeq -2(1-\beta)\overline{w}_1 \qquad \overline{w}_7 = -\beta\overline{w}_1 \qquad \overline{w}_8 \simeq -(3\beta-1)\overline{w}_1 . \tag{12}$$

The dominant reactions in the productions of these species are found to be 2 and 8; 3, 8 and 9; and 3 and 9, respectively. Hence, we finally arrive at

$$\beta \simeq \frac{1 + k_3/k_5}{3} \quad \frac{1 + (1+2\phi)^{1/2} + (k_5-k_3)\phi/(k_5+k_3)}{1 + (1+2\phi)^{1/2} + (1-k_3/k_5)\phi}$$

$$\simeq 0.49 \quad \frac{1 + (1+2\phi)^{1/2} + 0.37\phi}{1 + (1+2\phi)^{1/2} + 0.54\phi} \tag{13}$$

Equation (13) leads to overall rates of production of NH_3, N_2 and H_2, and overall heat of decomposition, to be used in the anaysis of a real hydrazine engine.

The preceding results are valid as long as $c_1/c = O(1)$. Euations (8) show however that as $c_1 \rightarrow 0$, both c_2 and c_3 become singular as $1/c_1$, and the analysis needs modification. For $c_1/c = O(10^{-1})$, reaction 1 may be neglected, while reactions 7 and 10 must be taken into account, the quasi-steady state of NH_2 and N_2H_3 being modified. We obtain

$$\overline{w}_1 \simeq -3 \frac{k_5}{k_8} (k_5-k_3)c^2 \left[1 + \frac{k_7(3k_5-k_3)}{k_2k_8} \frac{c}{c_1} + 4 \frac{k_3k_5k_{10}}{k_2^2k_8} \frac{c^2}{c_1^2} \right]^{-1}$$

$$\simeq -10^{14}\exp\left(-\frac{36000}{RT}\right)c^2 \left[1 + 64\exp\left(-\frac{11000}{RT}\right)\frac{c}{c_1} + 10^3\exp\left(-\frac{24000}{RT}\right)\frac{c^2}{c_1^2} \right]^{-1},$$

$$\tag{14}$$

$$\beta \simeq \frac{1 + k_3/k_5}{3} \quad \frac{1 + 2k_7(3k_5-k_3) c/k_2k_8(1+k_3/k_5) c_1}{1 + k_7(3k_5-k_3) c/k_2k_8 c_1}$$

$$\simeq 0.49 \quad \frac{1 + 87\exp(-11000/RT)c/c_1}{1 + 64\exp(-11000/RT)c/c_1}, \tag{15}$$

$$\frac{c_2}{c} = O(10^{-3}) , \quad \frac{c_3}{c} = O(10^{-5}) , \quad \frac{c_4}{c} = O(10^{-3}), \quad \frac{c_5}{c} = O(10^{-6}).$$

$$\tag{16}$$

Both c_2 and c_3 pass through a large maximum in this range of values of c_1, and the characteristic time for the overall reaction is now

much shorter, $(10^{-2}/P)$sec.

For $c_1/c = 0(10^{-2})$, the overall kinetics changes again. Reactions 7 and 8 may now be neglected, while reaction 1 must again be taken into account. The overall reaction time is again $(10^{-1}/P)$sec. We obtain

$$\frac{c_2}{c} = 0(10^{-4}), \quad \frac{c_3}{c} = 0(10^{-6}), \quad \frac{c_4}{c} = 0(10^{-5}), \quad \frac{c_5}{c} = 0(10^{-6}), \tag{17}$$

$$\beta \simeq 2/3 \tag{18}$$

$$\bar{w}_1 \simeq -\frac{3}{4}\frac{k_2^2}{k_{10}}\left(\frac{k_5}{k_3} - 1\right)c_1^2\frac{1}{2}\left[1 + \left\{1 + \frac{16k_1k_{10}k_3^2}{k_2^2(k_5-k_3)^2}\frac{c}{c_1}\right\}^{1/2}\right]$$

$$\simeq -10^{11}\exp\left(-\frac{12000}{RT}\right)c_1^2\frac{1}{2}\left[1 + \left\{1 + 2.7\times10^9\exp\left(-\frac{50000}{RT}\right)\frac{c}{c_1}\right\}^{1/2}\right], \tag{19}$$

It may be noticed that the limits of (9) and (14), for decreasing c_1/c and c/c_1 respectively, match each other smoothly as they should. Similarly the limits of (14) and (19), for decreasing c_1/c and c/c_1 respectively, match smoothly too. Similar statements may be made about (13) and (15), and (15) and (18). The results in (18) and (19) agree with those given by Urrutia in Ref.12 for $c_1/c = 0(10^{-2})$.

4. TEMPERATURE NEAR 800°K

For $T \simeq 800°K$ and $c_1 = 0(1)$ we find four stages in the decomposition. First, NH and H reach a quasi-steady state in a time of the order of $(10^{-6}/P)$sec, through reactions 5 and 6, and 3 and 4, respectively. Next, in a time of the order of $(10^{-5}/P)$sec, NH_2 comes to a quasi-steady state through reactions 1 and 2. That state is modified by reactions 4, 5 and 6 in a third stage, whose characteristic time is $(10^{-3}/P)$sec. Simultaneously there is exponential growth of N_2H_4, leading to a quasi-steady state through reactions 2, 3, 5, 6, 8 and 9, while reaction 8 modifies the equilibrium of H.

Transformation of hydrazine into products proceeds in a $(10/P)$sec time scale through reactions 2, 4 and 6; in this final stage reaction 1 may be neglected. The results for the overall reaction are

$$\frac{c_2}{c} = 0(10^{-6}), \quad \frac{c_3}{c} = 0(10^{-7}), \quad \frac{c_4}{c} = 0(10^{-4}), \quad \frac{c_5}{c} = 0(10^{-7}), \tag{20}$$

$$\simeq -1.2 \times 10^{14} \exp\left(- \frac{36000}{RT}\right) c^2 \left[1 + 0.8 \left\{1 + 5.1 \times 10^2 \exp\left(- \frac{11000}{RT}\right) \frac{c}{c_1}\right\}^{-1}\right], \tag{21}$$

$$\beta \simeq \frac{1 + k_3/k_5}{3} \left[1 + \frac{2k_3/3k_5}{1 + k_9(k_5-k_3)c/k_4 k_8 c_1}\right]^{-1}$$

$$\simeq 0.45 \left[1 + \frac{0.24}{1 + 5.1 \times 10^2 \exp(-11000/RT)c/c_1}\right]^{-1} \tag{22}$$

When $c_1 \to 0$, the overall kinetics changes because c_2 and c_3 become singular. For $c_1 = 0(10^{-1})$ reaction 7 must be taken into account, while reaction 4 may be neglected. We arrive at

$$\frac{c_2}{c} = 0(10^{-5}), \quad \frac{c_3}{c} = 0(10^{-6}), \quad \frac{c_4}{c} = 0(10^{-4}), \quad \frac{c_5}{c} = 0(10^{-7}), \tag{23}$$

$$\overline{w}_1 \simeq -3 \frac{k_5}{k_8} (k_5 - k_3)c^2 \left[1 + \frac{k_7(3k_5-k_3)}{k_2 k_8} \frac{c}{c_1}\right]^{-1}$$

$$\simeq -1.2 \times 10^{14} \exp\left(- \frac{36000}{RT}\right) c^2 \left[1 + 66 \exp\left(- \frac{11000}{RT}\right) \frac{c}{c_1}\right]^{-1} \tag{24}$$

$$\beta \simeq \frac{1 + k_3/k_5}{3} \frac{1 + 2k_7(3k_5-k_3)c/k_2 k_8(1+k_3/k_5)c_1}{1 + k_7(3k_5-k_3)c/k_2 k_8 c_1}$$

$$\simeq 0.45 \frac{1 + 97 \exp(-11000/RT)c/c_1}{1 + 66 \exp(-11000/RT)c/c_1} \tag{25}$$

As in the 1000°K case, both c_2 and c_3 pass through a large maximum in this range of values of c_1, and the overall characteristic time decreases sharply, to a $(1/P)$sec value.

For $c_1' = 0(10^{-2})$, reaction 8 may be neglected but reaction 10 must be taken into account. The overall reaction time is again $(10/P)$sec. We also find

$$\beta \simeq 2/3 , \tag{26}$$

$$\bar{w}_1 \simeq -3 \frac{k_5}{k_8}(k_5-k_3)c^2 \left[\frac{k_7(3k_5-k_3)}{k_2 k_8} \frac{c}{c_1} + 4 \frac{k_3 k_5 k_{10}}{k_2^2 k_8} \frac{c^2}{c_1^2}\right]^{-1}$$

$$\simeq -1.8 \times 10^{12} esp\left(-\frac{25000}{RT}\right)cc_1 \left[1 + 15 \ exp\left(-\frac{13000}{RT}\right)\frac{c}{c_1}\right]^{-1} , \tag{27}$$

$$\frac{c_2}{c} = 0(10^{-5}), \quad \frac{c_3}{c} = 0(10^{-6}), \quad \frac{c_4}{c} = 0(10^{-5}), \quad \frac{c_5}{c} = 0(10^{-7}). \tag{28}$$

Notice again the smooth matching of Eqs. (21), (24) and (27), and (22), (25) and (26).

5. CONCLUSION

Using an asymptotic analysis based on large differences among the rate constants of several elementary reactions, we have shown that the Eberstein-Glassman mechanism for the thermal decomposition of hydrazine leads to an overall kinetics at temperatures near 800°K and near 1000°K: Relaxation of the active radicals appearing in the decomposition occurs in several stages involving times extremely short compared with the characteristic time for the overall process of decomposition. This last time is of the order of $(10^{-1}/P)$sec (the pressure P being measured in atmospheres) for temperature, T, near 1000°K, and hydrazine molar fraction, c_1/c, of the order of either unity or 10^{-2}; that time is $(10^{-2}/P)$sec for $c_1/c = 0(10^{-1})$. For given c_1/c between unity and values $0(10^{-2})$, the overall time at $T \simeq 800°K$ is about 10^2 times larger than the overall time at 1000°K.

We have found explicit expressions (see Secs. 3 and 4) for the rate of decomposition of hydrazine $|\bar{w}_1|$, and the stoichiometric coefficient β, in the overall reaction

$$N_2 H_4 \rightarrow 2(1-\beta)NH_3 + \beta N_2 + (3\beta-1)H_2 .$$
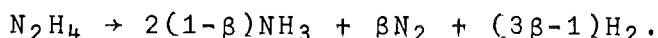
Once β is known, the heat of decomposition can be found from thermodynamic tables. At either 800 or 1000°K the expressions for w_1 (and β) change in form when c_1/c decreases from unity down to

values $O(10^{-1})$ and $O(10^{-2})$; we have shown however that the expressions for the different ranges of c_1/c match smoothly. Furthermore, it may be verified that for given $O(c_1/c)$, the expressions for $\overline{w}_1$ (and β) at $T \simeq 800°K$ and $T \simeq 1000°K$ match smoothly each other at intermediate temperatures *. Thus it is possible to write down patched formulae for $\overline{w}_1$ and β , valid for, say, $750°K < T < 1050°K$ and $1 \geq c_1/c > 10^{-3}$. It should be noticed however that such formulae are quite complex and involve errors of the order of 10 or 20%.

We are presently evaluating the extent of the validity of the Eberstein-Glassman mechanism taking into account, in particular, that reaction 1 is quasi-unimolecular, reaction 10 being the low-pressure limit of its inverse. We have already verified that the inverse reactions of reactions 2-9 may be neglected, except possibly in the case of reaction 5.

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* Compare Eqs. (9), (13)-(15), (18) and (19) in Sec.3 with Eqs. (21), (22), (24)-(27) in Sec.4, respectively. Differences between factors 10^{14} and 1.2×10^{14}, 0.45 and 0.49, etc. are due to our having approximated factors $(1-k_3/k_5)$, $(1+k_3/k_5)$, etc. by numbers independent of T, changing slightly from the neighborhood of $800°K$ to the neighborhood of $1000°K$.

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